The Use of Methyl Butyrate-Based Electrolytes with Additives to Enable the Operation of Li-Ion Cells with High Voltage Cathodes over a Wide Temperature Range

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Outline

- Introduction
- Objective
- Background
- Approach and Methodology

- Ester-Based Electrolytes for LFP, NCO and NCA-Based Systems
- Graphite-Toda $LiNiCoMnO_2$ System
- Graphite-Toda HE-5050 $LiNiCoMnO_2$ (Argonne Developed) System
  - Low Temperature Discharge Characterization
  - Electrochemical Characterization (Tafel, EIS)
  - Cycle Life Performance

- Conclusions

Outline

➢ **DOE desires Li-ion batteries than can operate over a wide temperature range *(i.e., -30 to +60^{o}C).* and provide good life characteristics for HEV and PHEV applications**

➢ **NASA also desires Li-ion batteries than can operate over a wide temperature range for future planetary lander and rover applications.**

Objectives and Approach

- ***Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -30 to +60^{o}C).***
- **Improve the high temperature stability and lifetime characteristics of wide operating temperature electrolytes.**
- **Define the performance limitations at low and high temperature extremes, as well as, life limiting processes.**
- **Demonstrate the performance of advanced electrolytes in large capacity prototype cells.**

Why Battery Performance Degrades at Low Temperatures?

- Increased cell and electrode polarizations in general
  - Ohmic, kinetic as well as mass transfer
- Increased Ohmic polarization
  - Mainly contributed by the electrolyte
    - Reduced Ionic mobility in electrolyte.
      - Slow diffusion of ions mainly due to increased viscosity of solvent components
    - Reduced ionic strength due to lower solubility at low temperatures.
- Slower electrode kinetics
  - Slower charge transfer at the electrodes governed by Arrhenius dependence.
  - Charge-transfer over film-covered electrodes?
- Enhanced mass transfer polarization
  - Slow diffusion of (Li^+) ion in solution caused by increased electrolyte viscosity
  - Slower diffusion of reactant/product species in the electrode lattices (bulk diffusion).
  - Surface films complicating the charge transfer and diffusion process.
- Likelihood of lithium plating is possible at high charge rates at low temperatures

Low Temperature Lithium Ion Electrolytes

Electrolyte Development: Approach/Background

General Approaches to Improve Low Temperature Performance of SOA Electrolytes

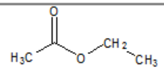
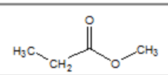
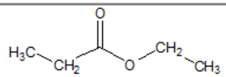
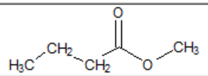
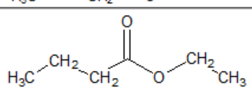
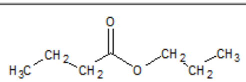
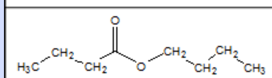
- Optimization of linear carbonate type and concentration
- Optimization of cyclic carbonate concentration (i.e., EC content)
- Use of aggressive low viscosity co-solvents
- Optimization of electrolyte salt type and concentration
- Use of "SEI promoting" additives

- These approaches are often used in conjunction to achieve desired result.
- In addition, the specific application can influence low temperature electrolyte selection (i.e., low temperature requirement, life requirement, or the need for high temperature resilience, etc.).

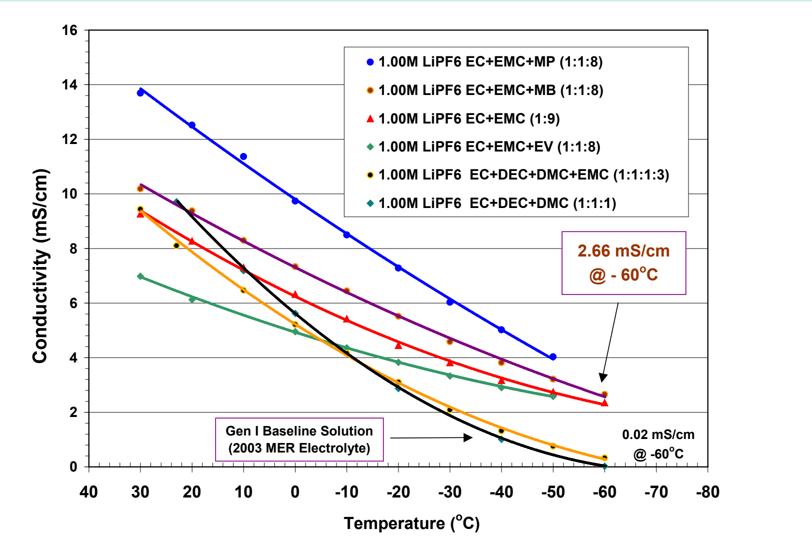
Low Viscosity, Low Melting Electrolyte Co-Solvents

Candidate High Molecular Weight Ester-Based Co-Solvents

Properties of Ester Co-Solvents

Chemical Structure	Name	m.p.	b.p	Viscosity (25°C)	Density	Dielectric Constant
	Ethyl acetate	-84°C	77°C		0.902	
	Methyl propionate	-87.5°C	79.8°C	0.431 cP	0.915	6.200
	Ethyl propionate	-73°C	99°C		0.888	
	Methyl butyrate	-85.8°C	102.8°C	0.541 cP	0.898	5.48
	Ethyl butyrate	-93°C	120°C	0.639 cP	0.878	5.18
	Propyl butyrate	-95.2°C	143°C		0.873	4.3
	Butyl butyrate	-91.5°C	164°C		0.829	

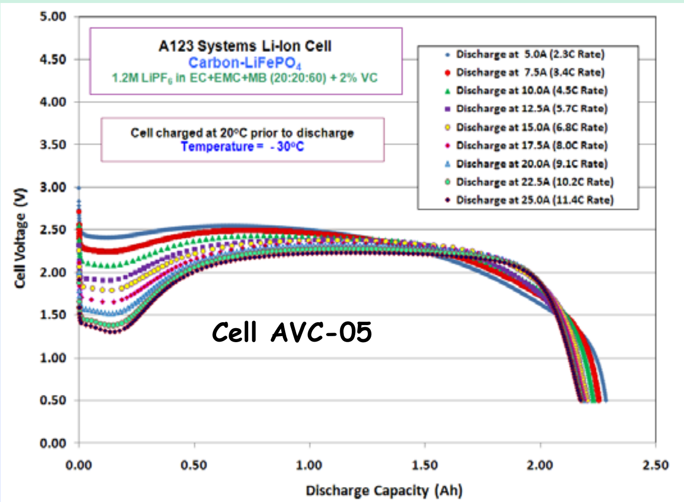
Ionic Conductivity of Ester Based Electrolytes

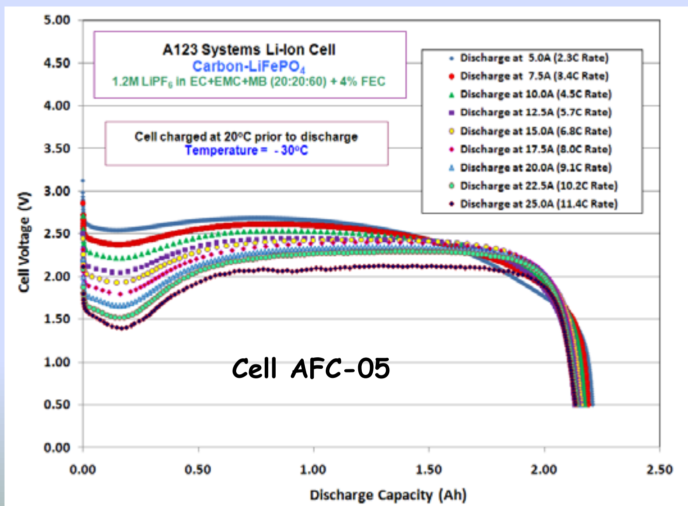


A123 2.20 Ah High Power LFP-Based Lithium-Ion Cells

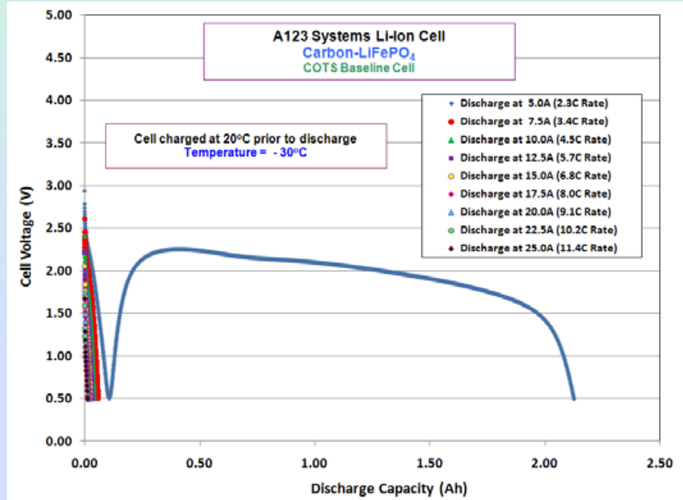
Discharge Rate Characterization Testing

Temperature = -30°C; Cells Discharged to 0.50V





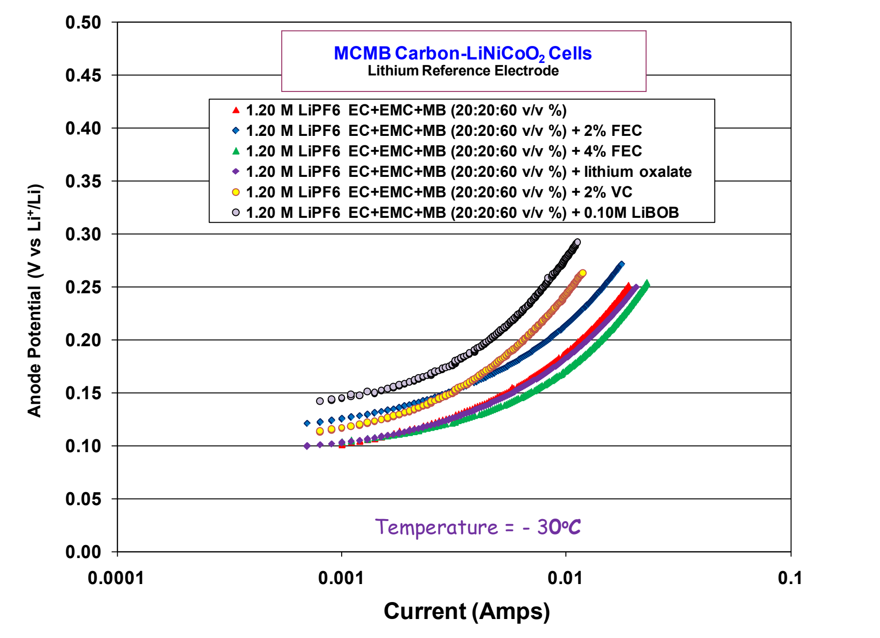
Baseline Electrolyte

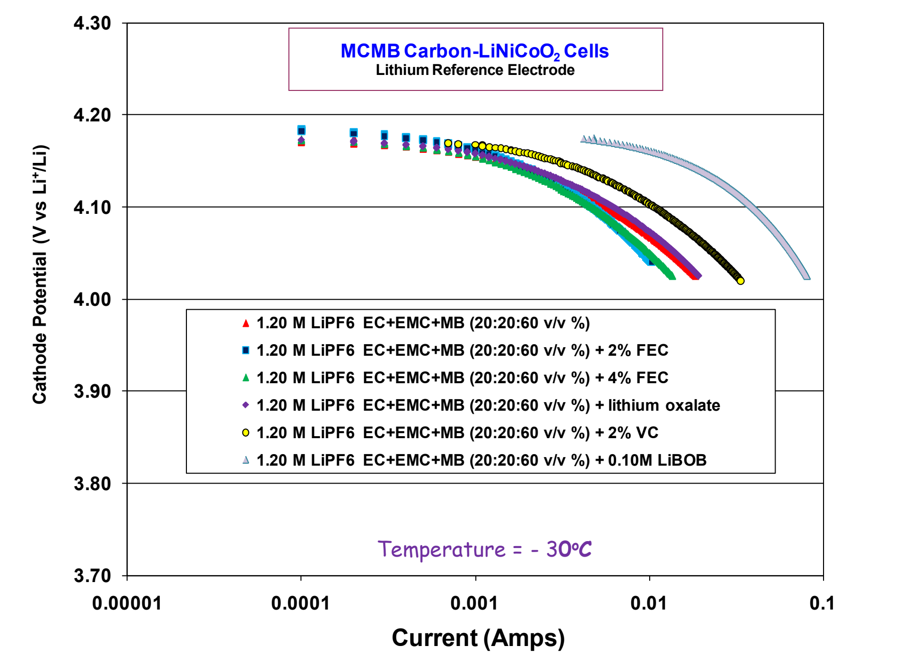


- The MB-based systems are capable of supporting greater than 11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.
  - Whereas, negligible capacity delivered with the baseline system under similar conditions.

M. C. Smart, A. S. Gozdz, L. D. Whitcanack, and B. V. Ratnakumar, 220th ECS Meeting, Boston, MA, October 11, 2011.

Experimental lithium-ion cells (MCMB-$LiNiCoO_2$) fabricated with **methyl butyrate**–based electrolytes containing various additives.



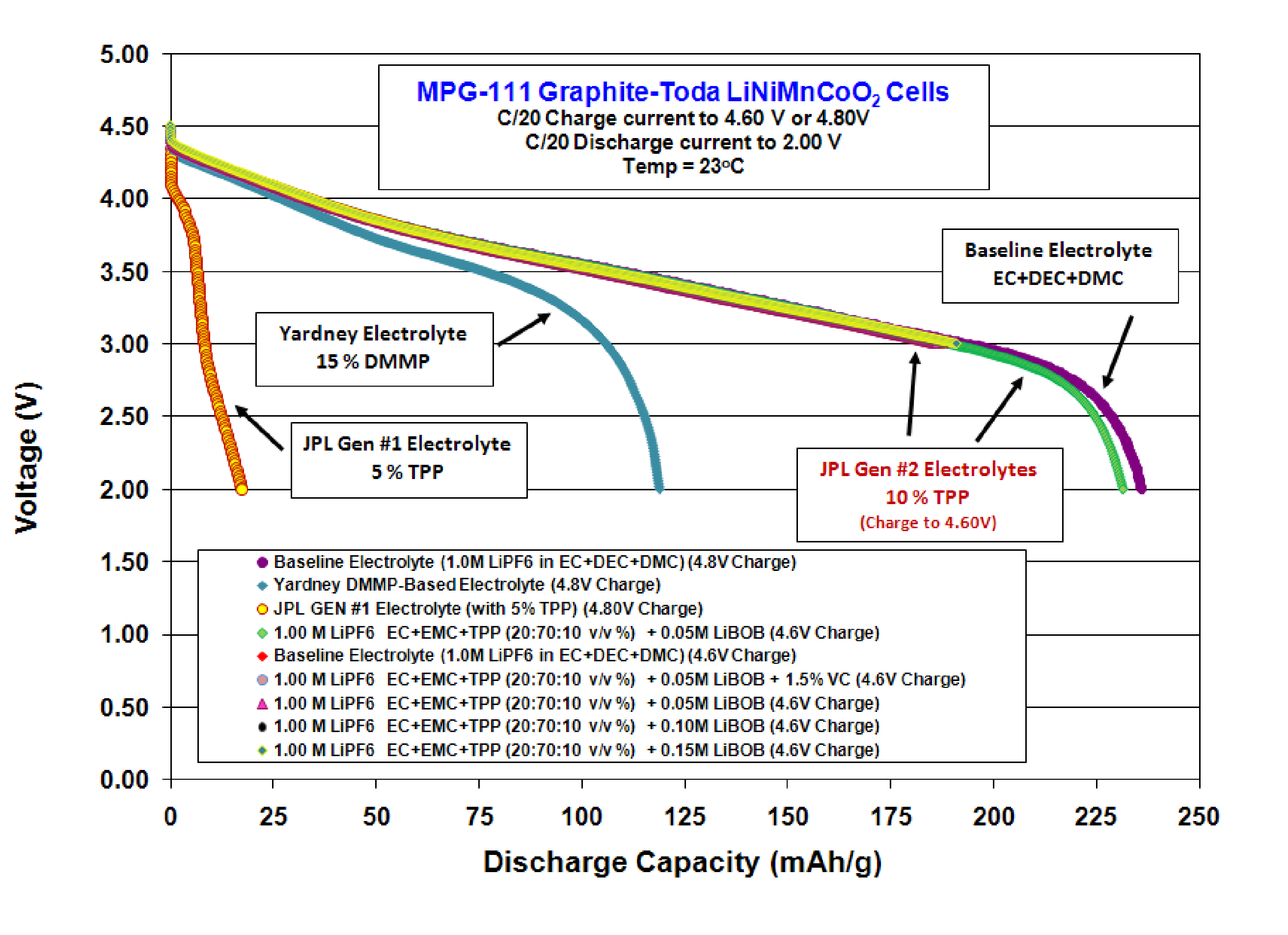


- **Promising electrolyte additives were explored in a wide operating temperature range solvent systems (EC+EMC+MB) with the intent of improving high temperature resilience.**
- **Some additives have the beneficial effect of improving the lithium kinetics through the formation of desirable SEI layers on both electrodes.**
- **LiBOB and VC were observed to improve the kinetics at the cathode, whereas FEC appears to improve the kinetics at the anode.**

M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, *J. Electrochem. Soc.*, **159 (6)**, A739-A751 (2012).

Electrolytes with Improved Safety for the MPG-111-Toda System

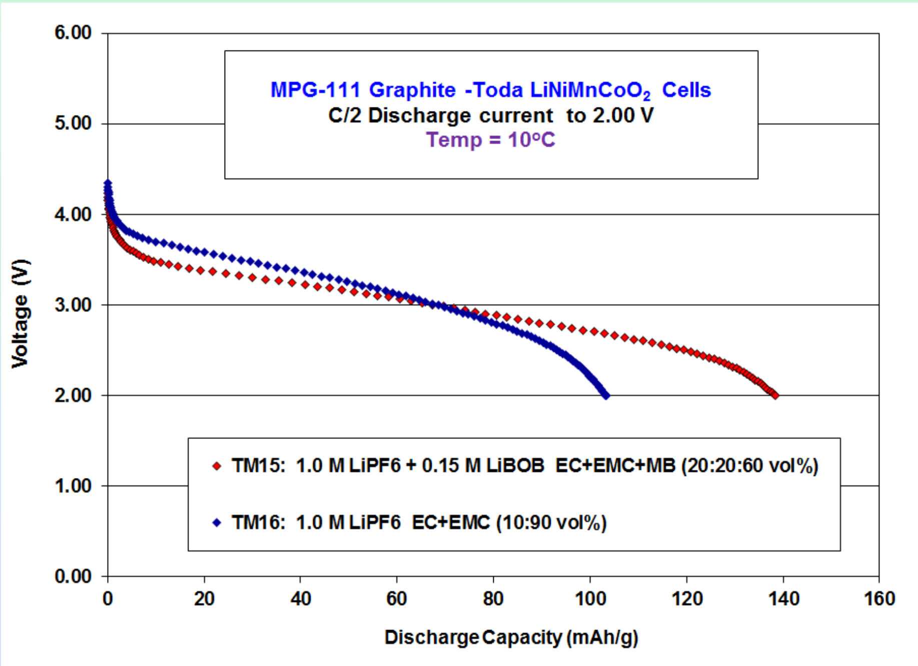
Comparison of Electrolyte Types (After Formation)



➢ ***The use of LiBOB dramatically improved the compatibility of TPP-containing electrolytes when coupled with high voltage NMC cathodes.***

M. C. Smart, F. C. Krause, C. Hwang, W. C. West, J. Soler, G. K. S. Prakash, and B. V. Ratnakumar, *ECS Trans.*, **35** (13), 1 (2011).

Characterization of Three Electrode
MPG-111 Graphite/Toda 9100 $LiNiCoMnO_2$ Cells

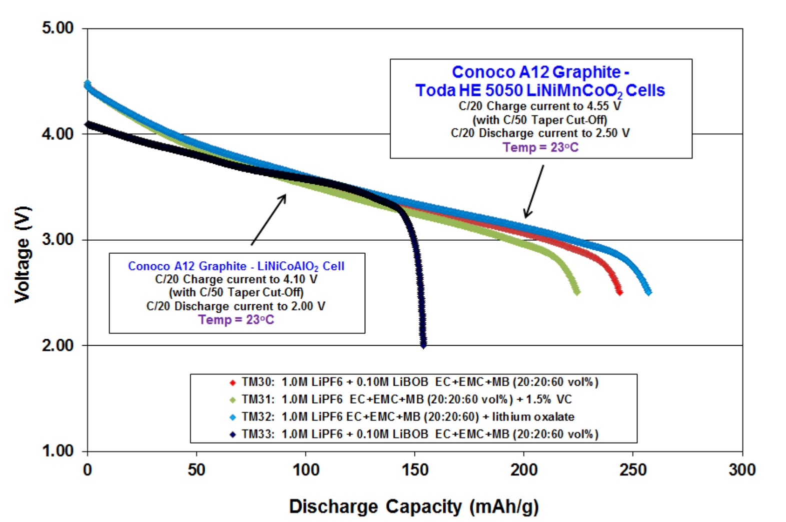


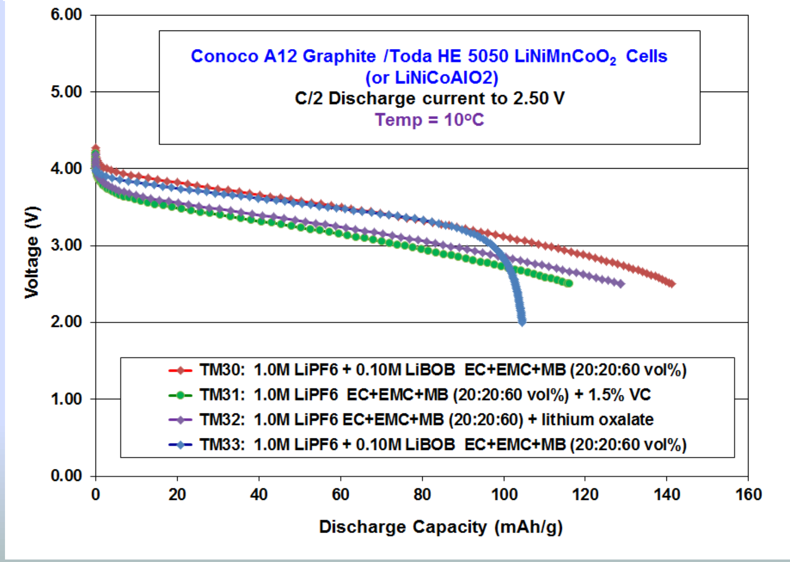
Electrolyte Type →		$1.0\ M\ LiPF_6 + 0.15\ M\ LiBOB$ EC+EMC+MB (20:20:60 vol%)			1.0 M LiPF6 EC+EMC (10:90 vol%)		
Temperature	Current (mA)	Capacity (Ah)	Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Capacity (mAh/g)	Percent (%)
23°C	C/20	0.3898	238.18	100.00	0.3920	239.85	100.00
	C/10	0.3639	222.36	93.36	0.3718	227.54	94.87
	C/5	0.3351	204.77	85.97	0.3398	207.94	86.70
	C/2	0.2815	172.00	72.21	0.2321	142.04	59.22
10°C	C/20	0.3289	200.97	84.38	0.2998	183.44	76.48
	C/10	0.3159	193.00	81.03	0.2952	180.65	75.32
	C/5	0.2841	173.55	72.87	0.2569	157.18	65.53
	C/2	0.2264	138.36	58.09	0.1688	103.29	43.06
'0°C	C/20	0.2912	177.92	74.70	0.2680	164.00	68.38
	C/10	0.2725	166.51	69.91	0.2606	159.49	66.50
	C/5	0.2393	146.23	61.40	0.2068	126.53	52.75
	C/2	0.1839	112.35	47.17	0.1247	76.28	31.80

- **The MB-based electrolyte displays improved rate capability at low temperature compared to an all carbonate-based formulation.**
- **Electrochemical measurements suggest that the cathode kinetics is dominating the poor rate capability at low temperature rather then electrolyte type.**
- **Improved low temperature rate capability will most likely be achieved with lower loading cathode (resulting in diminished specific energy of the cell).**

Characterization of Three Electrode Conoco Graphite/ Toda HE5050 $LiNiCoMnO_2$ Cells

Electrolyte Type	Charge Capacity (mAh/g) 1st Cycle	Discharge Capacity (mAh/g) 1st Cycle	Irreversible Capacity (mAh/g) (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Reversible Capacity (mAh/g) 5th Cycle	Cummulative Irreversible Capacity (mAh/g) (1st-5th Cycle)	Cathode Type
1.0M LiPF6 + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)	323.57	246.10	77.47	76.06	243.87	138.98	Argonne NMC (Toda HE 5050)
1.0M LiPF6 EC+EMC+MB (20:20:60 vol%) + 1.5% VC	325.89	233.46	92.43	71.64	224.33	211.93	Argonne NMC (Toda HE 5050)
1.0M LiPF6 EC+EMC+MB (20:20:60) + lithium oxalate	337.29	261.84	75.45	77.63	257.10	125.28	Argonne NMC (Toda HE 5050)
1.0M LiPF6 + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)	182.62	161.05	21.57	88.19	153.90	91.64	Argonne NCA ($LiNiCoAlO_2$)





- A number of methyl butyrate-based electrolytes have been evaluated in the high voltage system involving the LLC-NMC (received from Argonne) and compared with a baseline NCA system.
- The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.
- At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.

Characterization of Three Electrode Conoco Graphite/ Toda HE5050 $LiNiCoMnO_2$ Cells

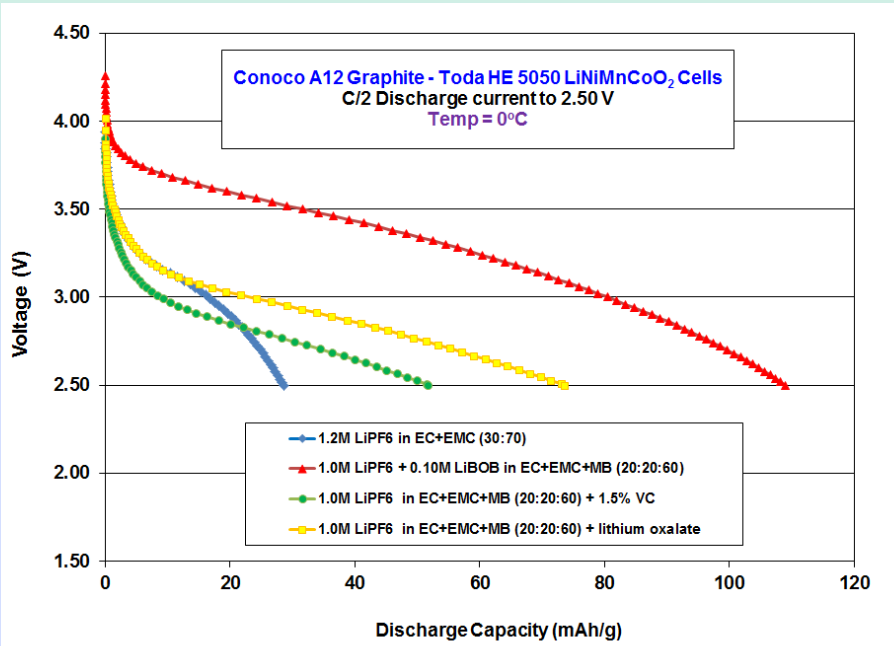
Electrolyte Type →		1.0M $LiPF_6$ + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)			1.0M $LiPF_6$ EC+EMC+MB (20:20:60 vol%) + 1.5% VC			1.0M $LiPF_6$ EC+EMC+MB (20:20:60) + lithium oxalate			1.2M $LiPF_6$ EC+EMC (30:70 vol%)		
Temperature	Current (mA)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)
23°C	C/20	0.1100	243.87	100.00	0.1018	224.33	100.00	0.1168	257.10	100.00	0.1211	266.57	100.00
	C/10	0.1059	234.95	96.34	0.1001	220.53	98.31	0.1130	248.60	96.69	0.1108	243.84	91.47
	C/5	0.0973	215.91	88.54	0.0947	208.66	93.01	0.1039	228.57	88.90	0.1029	226.42	84.94
	C/2	0.0843	186.92	76.65	0.0840	185.03	82.48	0.0900	197.97	77.00	0.0896	197.16	73.96
10°C	C/20	0.0972	215.59	88.40	0.0829	182.73	81.45	0.0974	214.33	83.37	0.1037	228.15	85.58
	C/10	0.0911	201.99	82.82	0.0798	175.82	78.37	0.0894	196.81	76.55	0.0858	188.84	70.84
	C/5	0.0798	177.06	72.60	0.0717	158.05	70.46	0.0798	175.55	68.28	0.0599	131.77	49.43
	C/2	0.0636	141.14	57.88	0.0526	116.01	51.71	0.0585	128.72	50.07	0.0335	73.81	27.69
	C/2	0.0642	142.39	58.39	0.0500	110.25	49.15	0.0567	124.85	48.56	0.0360	79.11	29.68
0°C	C/20	0.0848	187.98	77.08	0.0668	147.14	65.59	0.0808	177.86	69.18	0.0748	164.70	61.78
	C/10	0.0745	165.15	67.72	0.0559	123.14	54.89	0.0670	147.33	57.30	0.0349	76.85	28.83
	C/5	0.0646	143.21	58.72	0.0467	102.91	45.88	0.0559	123.02	47.85	0.0250	55.12	20.68
	C/2	0.0491	108.92	44.66	0.0235	51.71	23.05	0.0334	73.53	28.60	0.0130	28.57	10.72

- A The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.
- At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.

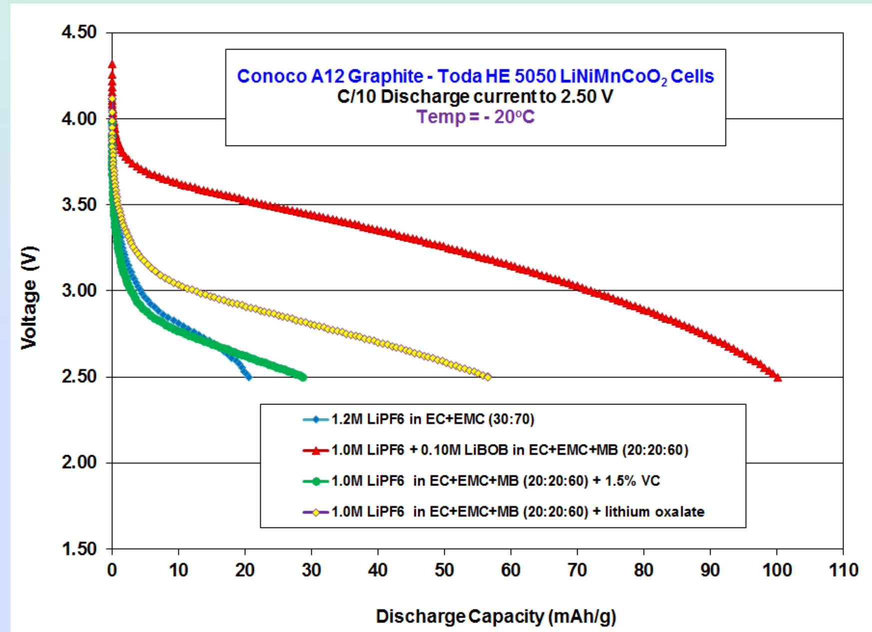
Characterization of Three Electrode Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Discharge Performance at Low Temperatures

C/2 Discharge at 0°C



C/10 Discharge at - 20°C

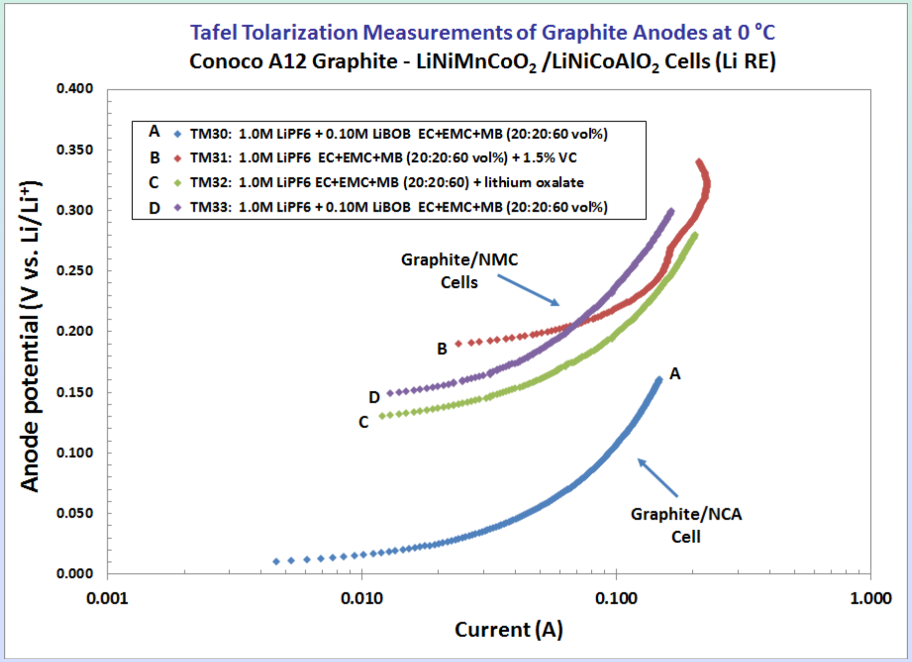


- Of the electrolytes evaluated, the MB-based system with LiBOB consistently displayed the best low temperature performance, which is attributed to (i) to improved kinetics at the cathode and to a lesser extent (ii) improved ionic conductivity of the electrolyte at low temperature.

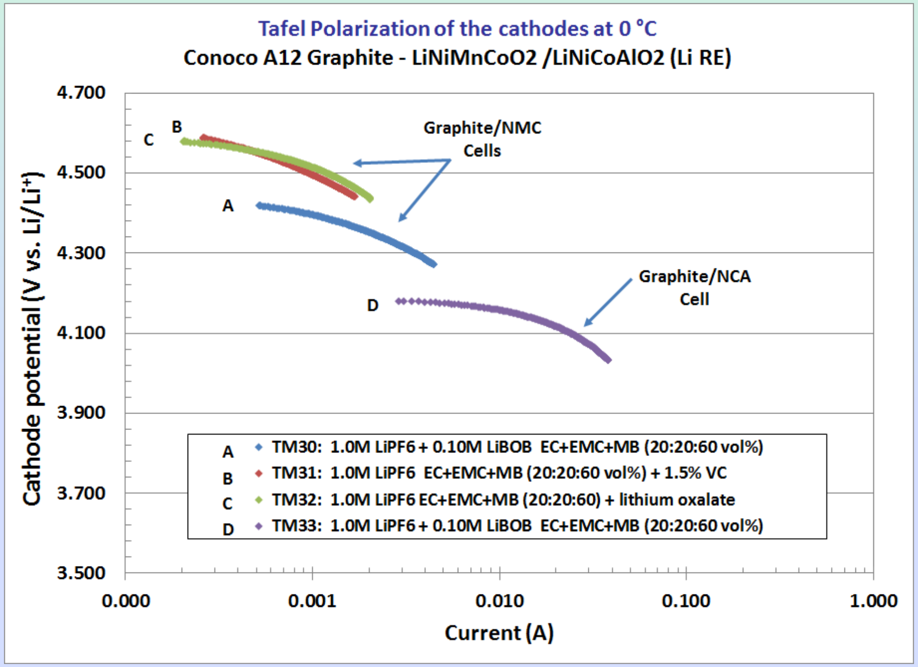
Characterization of Three Electrode Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Tafel Polarization Measurements at 0°C

Conoco Graphite Electrode Measurements



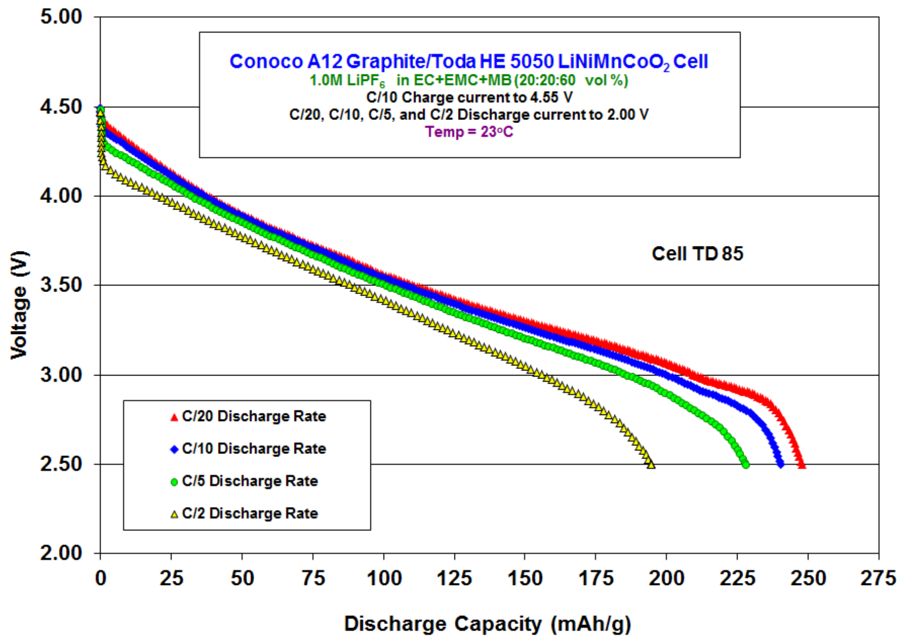
NCA and NCM Electrode Measurements



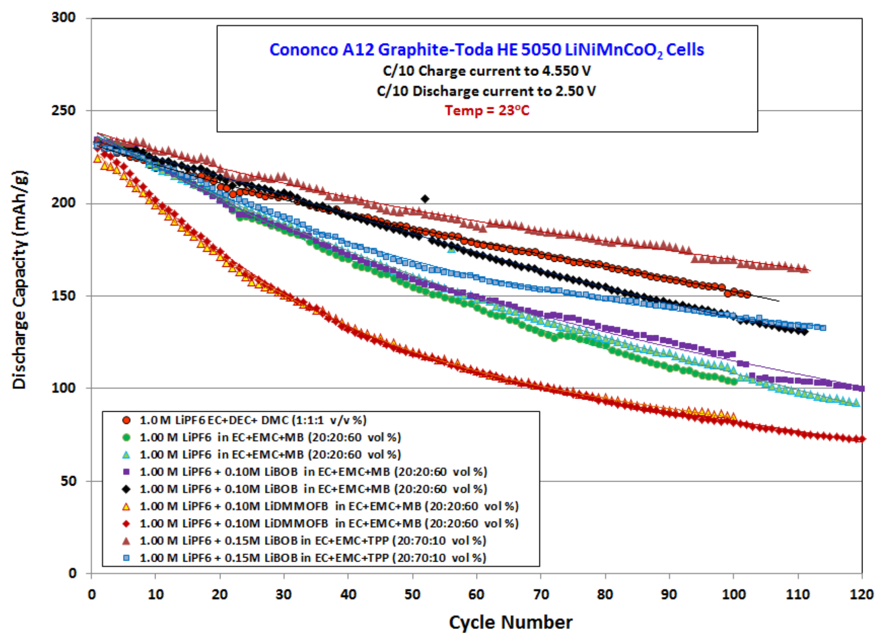
- When Tafel polarization measurements were performed each electrode (using 3-electode cells), both the NCA and NMC electrodes displayed poorer lithium kinetics compared to the anode.
- Of the different cathodes, the LLC-NMC electrodes (received from Argonne) displayed much lower lithium de-intercalation kinetics compared to the NCA electrodes (attributed to poor charge transfer resistance of the electrodes), which is exacerbated at lower temperatures.
- Of the electrolytes evaluated, the MB-based system with LiBOB displayed the best cathode kinetics.

Characterization of Conoco Graphite/ Toda HE5050 $LiNiCoMnO_2$ Coin Cells

Discharge Rate Capability at 23°C



Cycle Life Performance at 23°C



- The discharge rate capability and cycle life performance of a number of cells containing methyl butyrate-based electrolytes was also evaluated at 23°C in coin cells .
- The presence of LiBOB in the methyl butyrate-based systems was observed to improve the cycle life characteristics.
- An electrolyte with low flammability containing triphenyl phosphate, was observed to provide improved cycle life performance compared to the baseline.

Characterization of Experimental Three-Electrode and Coin Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

- Prepared a number of three electrode cells and coin cells containing methyl butyrate (MB)-based electrolytes containing various additives.
- The additives are anticipated to improve the high temperature resilience and, in some cases, improve the kinetics at low temperature.
- The additives include:
  - Lithium difluoro(oxalato)borate (LiDFOB)
  - Lithium bis(oxalato)borate (LiBOB)
  - Lithium 4,5-dicyano-2-(trifluoromethyl)imidazole (LiTDI)
  - Lithium tetrafluoroborate (LiBF4)
  - Di-t-butyl-pyrocarbonate (DBPC)
- The LiDFOB and LiTDI additives have been provided to us by Prof. Wesley Henderson's group (North Carolina State University).
- The results of these studies will be compared and contrast with the previous work performed on graphite/HE 5050 NMC materials.

Characterization of Experimental Three-Electrode and Coin Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

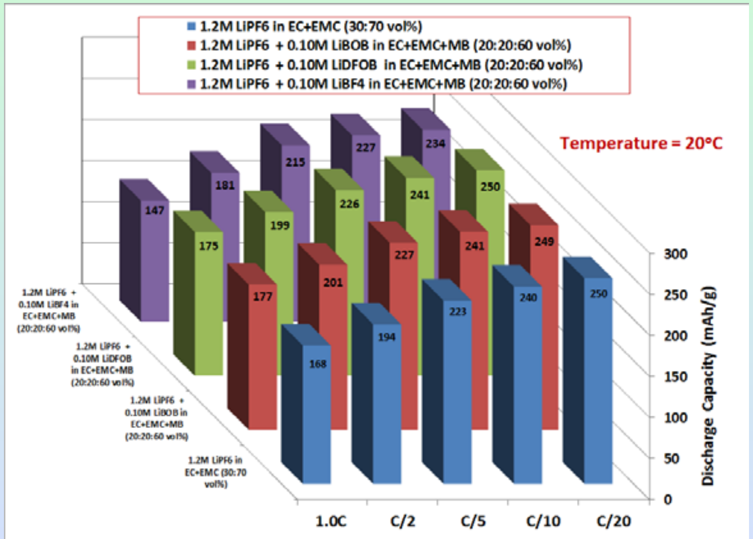
Cell Number	Electrolyte Type	Cell Type	Cathode Active Weight (g)	Charge Capacity (mAh) 1st Cycle	Discharge Capacity (mAh) 1st Cycle	Discharge Capacity (mAh/g) 1st Cycle	Irreverisible Capacity (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Charge Capacity (mAh) 5th Cycle	Reversible Capacity (mAh) 5th Cycle	Reversible Capacity (mAh/g) 5th Cycle	Cummulative Irreverisible Capacity (1st-5th Cycle) (mAh)	Cummulative Irreverisible Capacity (1st-5th Cycle) (mAh/g)	Couloumbic Efficiency (5th Cycle)
MB01	1.20M $LiPF_6$ in EC+EMC (30:70 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0126	4.0044	3.2022	255.04	0.802	79.97	3.1766	3.1555	251.31	0.8728	69.51	99.33
MB01	1.20M $LiPF_6$ in EC+EMC (30:70 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0126	4.0846	3.2513	258.94	0.833	79.60	3.2232	3.2084	255.53	0.8933	71.15	99.54
MB03	1.20M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0126	3.9959	3.2194	256.40	0.776	80.57	3.1628	3.1383	249.94	0.8785	69.97	99.23
MB04	1.20M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0127	4.0355	3.2391	254.49	0.796	80.26	3.1857	3.1689	248.97	0.8678	68.18	99.47
MB05	1.20M $LiPF_6$ + 0.10M LiDFOB in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0127	4.0799	3.2225	253.19	0.857	78.99	3.2265	3.1895	250.59	1.0148	79.73	98.85
MB06	1.20M $LiPF_6$ + 0.10M LiDFOB in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0128	4.0971	3.2254	251.71	0.872	78.72	3.1991	3.1666	247.12	1.0195	79.56	98.98
MB07	1.20M $LiPF_6$ + 0.10M $LiBF_4$ in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0128	4.1172	3.2253	251.70	0.892	78.34	3.2228	3.1266	244.00	1.1665	91.03	97.01
MB08	1.20M $LiPF_6$ + 0.10M $LiBF_4$ in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0129	4.14602	3.26416	253.04	0.882	78.73	3.2781	3.1875	247.09	1.1467	88.89	97.24
MB09	1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 vol%) + 2.0% DBPC	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0129	3.55990	2.14506	166.28	1.415	60.26	2.0668	1.9676	152.53	1.9759	153.17	95.20
MB10	1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 vol%) + 2.0% DBPC	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0130	3.50146	1.99914	153.95	1.502	57.09	1.9279	1.8249	140.53	2.0422	157.26	94.66
MB11	1.20M $LiPF_6$ + 0.10M LiTDI in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0130	4.28841	2.91851	224.74	1.370	68.06	3.2501	3.1753	244.52	1.9470	149.93	97.70
MB12	1.20M $LiPF_6$ + 0.10M LiTDI in EC+EMC+MB (20:20:60 vol%)	Graphite/Toda HE 5050 $LiNiMnCoO_2$	0.0131	4.31816	2.97833	227.84	1.340	68.97	3.2807	3.1989	244.71	1.9477	149.00	97.51

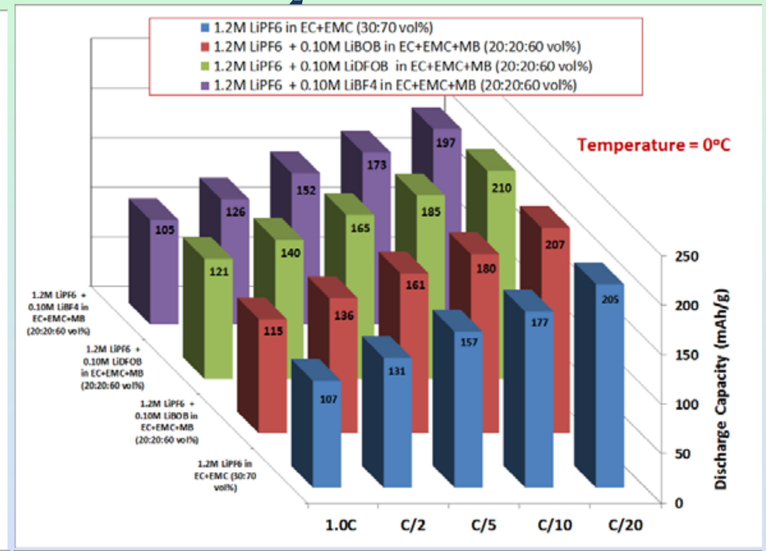
Low Temperature Characterization of Experimental Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Coin Cells

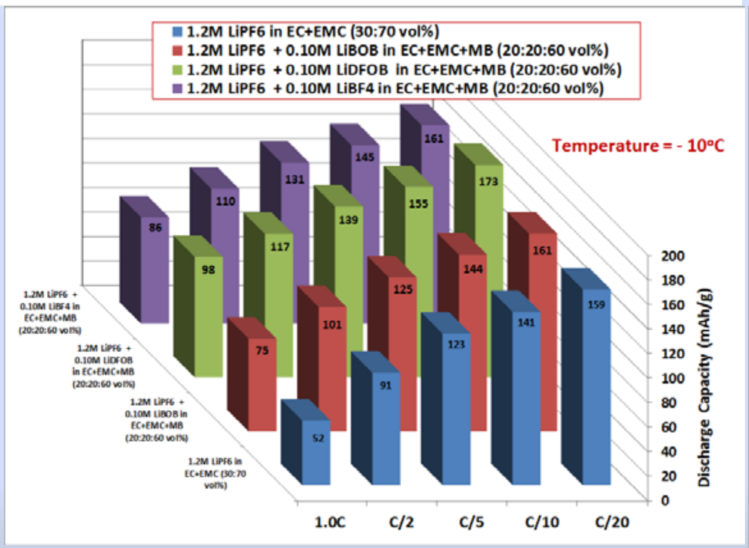
		MB01			MB03			MB05			MB07		
Electrolyte Type →		1.2M $LiPF_6$ in EC+EMC (30:70 vol%)			1.2M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MB (20:20:60 vol%)			1.2M $LiPF_6$ + 0.10M LiDFOB in EC+EMC+MB (20:20:60 vol%)			1.2M $LiPF_6$ + 0.10M $LiBF_4$ in EC+EMC+MB (20:20:60 vol%)		
Temperature	Discharge Rate	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)
20°C	C/20	0.00314	250.03	100.00	0.00312	248.72	100.00	0.00318	249.75	100.00	0.00299	233.62	100.00
	C/10	0.00301	239.61	95.83	0.00302	240.89	96.85	0.00306	240.59	96.33	0.00290	226.70	97.04
	C/5	0.00280	222.76	89.09	0.00286	227.50	91.47	0.00287	225.70	90.37	0.00275	214.57	91.85
	C/2	0.00244	193.96	77.57	0.00252	200.57	80.64	0.00253	198.77	79.59	0.00232	180.99	77.47
	1.0C	0.00211	168.30	67.31	0.00222	176.57	70.99	0.00222	174.60	69.91	0.00189	147.42	63.10
0°C	C/20	0.00257	204.92	81.96	0.00260	207.01	83.23	0.00267	209.53	83.89	0.00252	196.98	84.32
	C/10	0.00223	177.30	70.91	0.00227	180.41	72.53	0.00235	184.78	73.98	0.00222	173.41	74.23
	C/5	0.00197	157.06	62.82	0.00202	161.21	64.81	0.00210	165.35	66.21	0.00195	152.40	65.24
	C/2	0.00164	130.60	52.23	0.00171	135.97	54.67	0.00178	140.00	56.05	0.00162	126.16	54.00
	1.0C	0.00135	107.44	42.97	0.00144	114.84	46.17	0.00154	120.93	48.42	0.00135	105.23	45.04
- 10°C	C/20	0.00200	159.13	63.64	0.00202	160.81	64.66	0.00220	172.89	69.22	0.00207	161.32	69.05
	C/10	0.00177	140.84	56.33	0.00180	143.70	57.77	0.00197	155.02	62.07	0.00186	145.12	62.12
	C/5	0.00155	123.25	49.29	0.00157	125.08	50.29	0.00177	139.03	55.67	0.00168	130.98	56.07
	C/2	0.00115	91.47	36.58	0.00127	100.97	40.60	0.00149	116.77	46.75	0.00141	109.67	46.94
	1.0C	0.00066	52.47	20.98	0.00095	75.32	30.28	0.00125	98.01	39.24	0.00111	86.35	36.96
- 20°C	C/20	0.00151	120.57	48.22	0.00152	121.39	48.81	0.00171	134.51	53.86	0.00163	127.49	54.57
	C/10	0.00132	105.21	42.08	0.00137	109.31	43.95	0.00156	122.25	48.95	0.00147	115.05	49.25
	C/5	0.00099	78.72	31.48	0.00117	93.27	37.50	0.00137	107.50	43.04	0.00128	99.79	42.72
	C/2	0.00052	41.40	16.56	0.00080	64.00	25.73	0.00109	85.96	34.42	0.00096	74.92	32.07
	1.0C	0.00018	14.59	5.84	0.00039	31.43	12.64	0.00082	64.33	25.76	0.00059	45.93	19.66

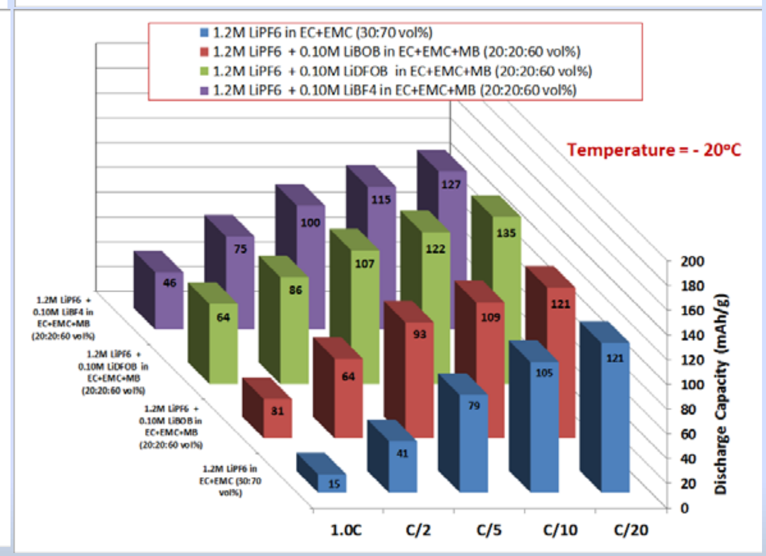
All cells charged at the respective temperature prior to discharge

Low Temperature Characterization of Experimental Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Coin Cells





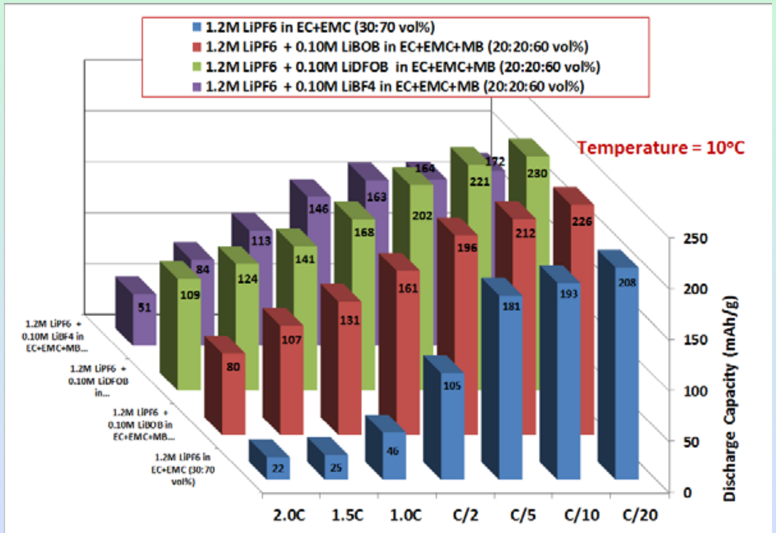


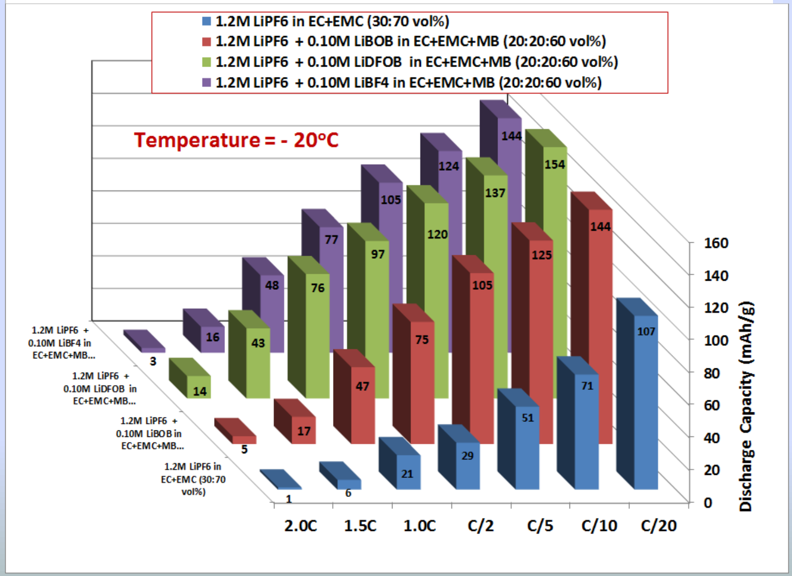


All cells charged at the respective temperature prior to discharge

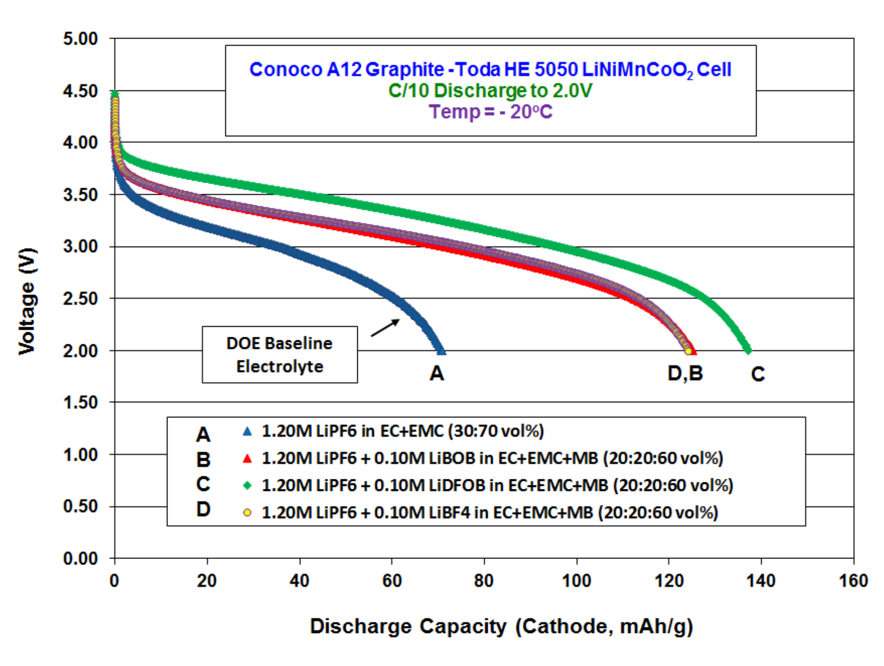
Characterization of Experimental Three-Electrode and Coin Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

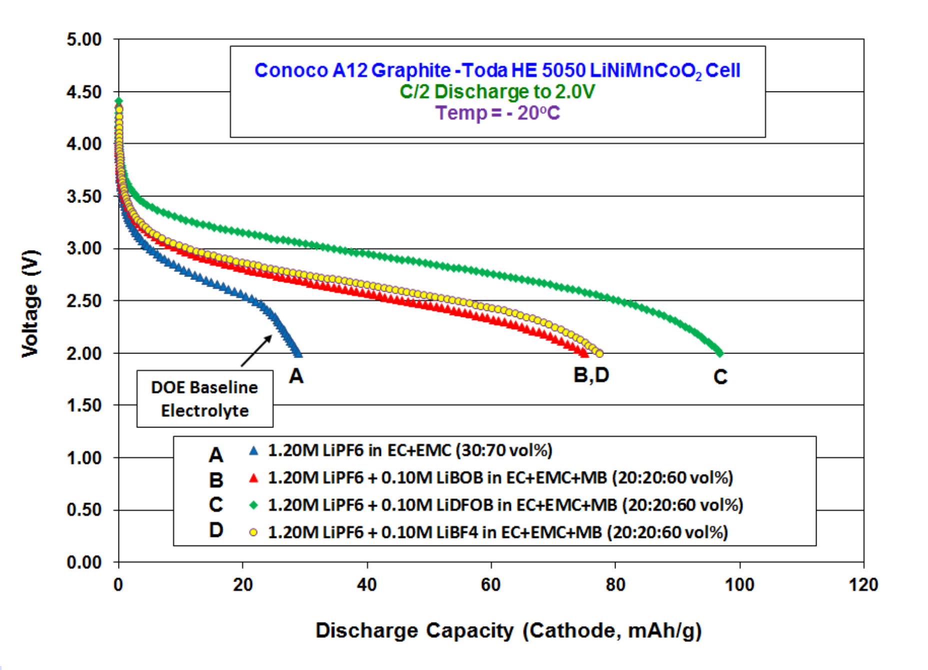
		MB01			MB03			MB05			MB07		
Electrolyte Type →		1.2M $LiPF_6$ in EC+EMC (30:70 vol%)			1.2M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MB (20:20:60 vol%)			1.2M $LiPF_6$ + 0.10M LiDFOB in EC+EMC+MB (20:20:60 vol%)			1.2M $LiPF_6$ + 0.10M $LiBF_4$ in EC+EMC+MB (20:20:60 vol%)		
Temperature	Discharge Rate	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)	Capacity (Ah)	Cathode Capacity (mAh/g)	Percent (%)
20°C	C/20	0.00314	250.03	100.00	0.00312	248.72	100.00	0.00318	249.75	100.00	0.00299	233.62	100.00
	C/10	0.00301	239.61	95.83	0.00302	240.89	96.85	0.00306	240.59	96.33	0.00290	226.70	97.04
	C/5	0.00280	222.76	89.09	0.00286	227.50	91.47	0.00287	225.70	90.37	0.00275	214.57	91.85
	C/2	0.00244	193.96	77.57	0.00252	200.57	80.64	0.00253	198.77	79.59	0.00232	180.99	77.47
	1.0C	0.00211	168.30	67.31	0.00222	176.57	70.99	0.00222	174.60	69.91	0.00189	147.42	63.10
+ 10°C	C/20	0.00261	208.24	83.28	0.00284	225.88	90.82	0.00293	229.89	92.05	0.00220	171.91	73.59
	C/10	0.00242	193.05	77.21	0.00267	212.26	85.34	0.00282	221.35	88.63	0.00210	163.53	70.00
	C/5	0.00227	180.89	72.34	0.00246	196.11	78.85	0.00257	201.61	80.73	0.00208	162.51	69.56
	C/2	0.00131	104.65	41.86	0.00203	161.36	64.87	0.00214	168.17	67.34	0.00188	146.45	62.69
	1.0C	0.00058	46.33	18.53	0.00165	131.08	52.70	0.00180	141.47	56.64	0.00145	113.12	48.42
	1.5C	0.00031	24.52	9.81	0.00135	107.36	43.16	0.00158	124.09	49.69	0.00108	84.36	36.11
	2.0C	0.00028	22.39	8.96	0.00101	80.05	32.18	0.00139	109.34	43.78	0.00065	50.60	21.66
0°C	C/20	0.00249	198.18	79.26	0.00264	210.19	84.51	0.00280	219.72	87.97	0.00238	185.99	79.61
	C/10	0.00226	180.18	72.06	0.00234	186.35	74.92	0.00249	195.41	78.24	0.00222	173.06	74.08
	C/5	0.00198	157.94	63.17	0.00208	165.81	66.67	0.00220	172.70	69.15	0.00203	158.14	67.69
	C/2	0.00117	92.81	37.12	0.00172	136.69	54.96	0.00183	143.86	57.60	0.00163	126.91	54.32
	1.0C	0.00033	26.41	10.56	0.00135	107.20	43.10	0.00153	120.10	48.09	0.00123	96.22	41.19
	1.5C	0.00024	18.86	7.54	0.00102	81.38	32.72	0.00131	102.76	41.14	0.00082	63.93	27.36
	2.0C	0.00018	14.60	5.84	0.00059	47.11	18.94	0.00109	85.48	34.23	0.00033	25.40	10.87
- 10°C	C/20	0.00216	171.82	68.72	0.00222	177.17	71.23	0.00235	184.47	73.86	0.00221	172.59	73.88
	C/10	0.00165	131.39	52.55	0.00200	159.25	64.03	0.00211	166.02	66.48	0.00200	155.75	66.67
	C/5	0.00101	80.73	32.29	0.00174	138.24	55.58	0.00183	144.16	57.72	0.00167	130.59	55.90
	C/2	0.00042	33.27	13.31									
	1.0C	0.00022	17.85	7.14	0.00090	71.89	28.90	0.00123	96.62	38.68	0.00091	71.37	30.55
	1.5C	0.00016	12.61	5.04	0.00053	42.29	17.00	0.00099	77.56	31.05	0.00044	34.51	14.77
	2.0C	0.00008	6.26	2.51	0.00021	16.82	6.76	0.00058	45.91	18.38	0.00013	9.80	4.19
- 20°C	C/20	0.00134	106.80	42.71	0.00181	144.03	57.91	0.00197	154.48	61.85	0.00185	144.29	61.77
	C/10	0.00089	70.75	28.30	0.00157	125.13	50.31	0.00175	137.13	54.91	0.00159	124.12	53.13
	C/5	0.00064	50.99	20.40	0.00132	105.03	42.23	0.00153	119.99	48.04	0.00134	104.63	44.79
	C/2	0.00036	28.86	11.54	0.00094	75.09	30.19	0.00123	96.86	38.78	0.00099	77.32	33.10
	1.0C	0.00027	21.16	8.46	0.00059	47.20	18.98	0.00097	76.45	30.61	0.00061	47.66	20.40
	1.5C	0.00008	5.98	2.39	0.00021	16.65	6.69	0.00055	43.13	17.27	0.00021	16.01	6.85
	2.0C	0.00002	1.30	0.52	0.00006	4.77	1.92	0.00017	13.74	5.50	0.00004	2.97	1.27



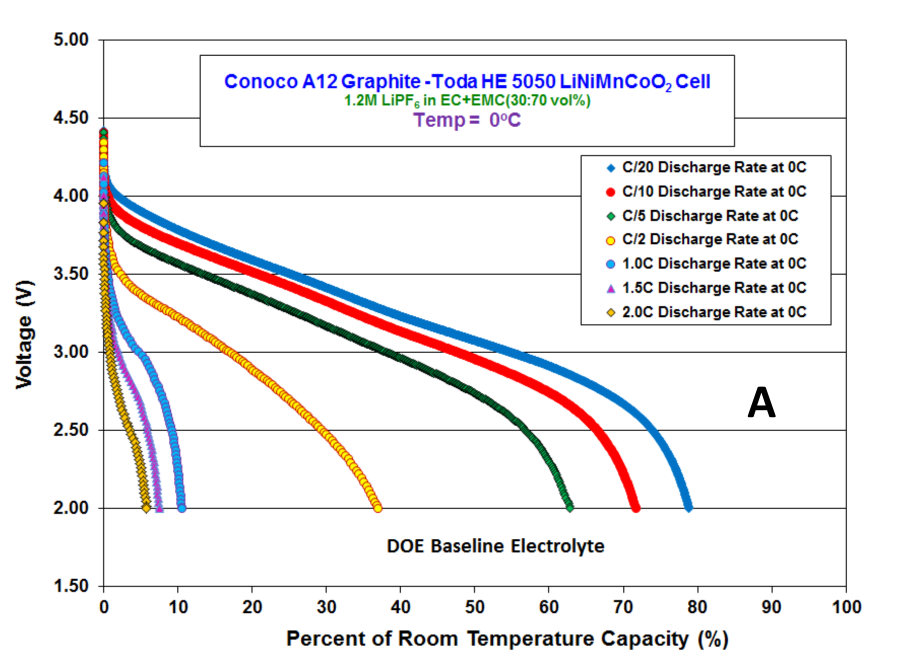


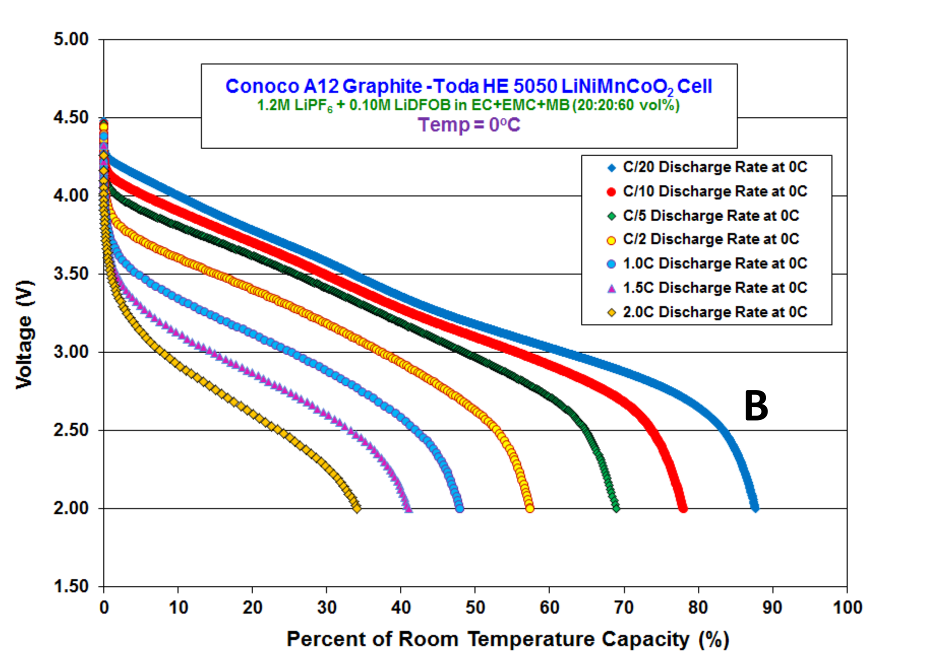
Low Temperature Characterization of Experimental Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Coin Cells





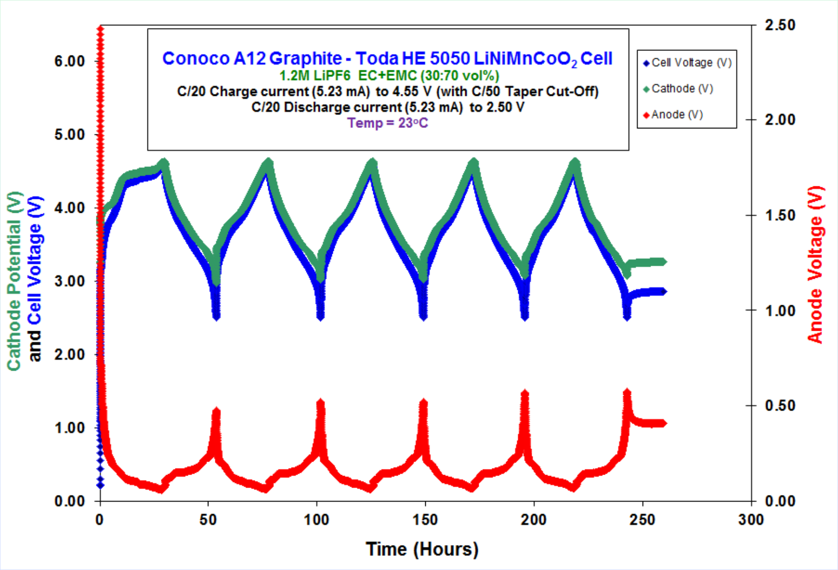
Low Temperature Characterization of Experimental Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Coin Cells





Tafel Characterization of Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Jelly Roll Three-Electrode Cells



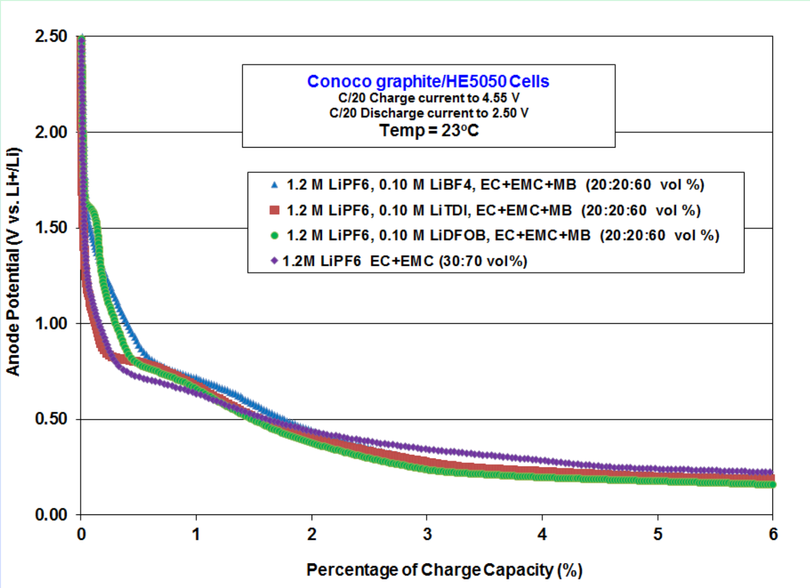
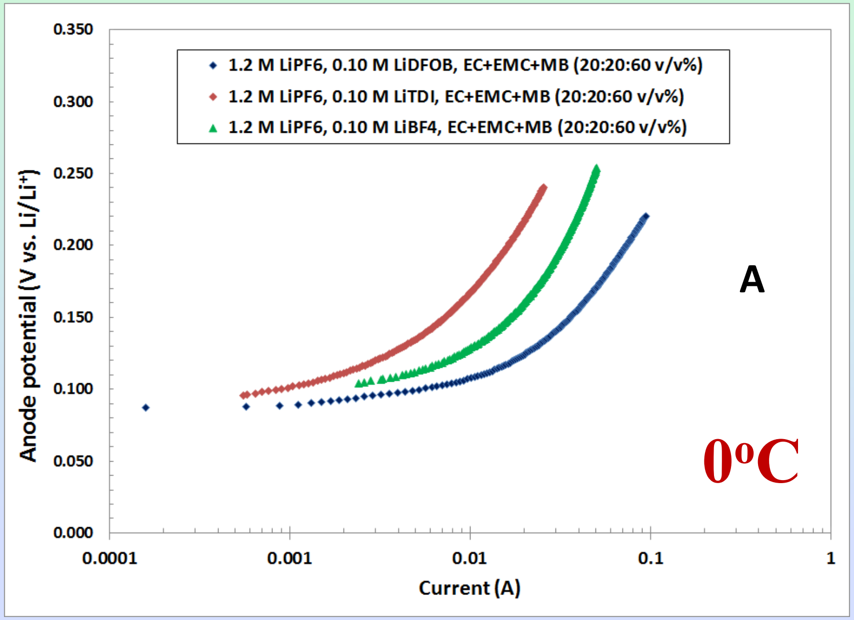


Figure: Tafel polarization measurements performed on Conoco graphite anodes (A) and NMC cathodes (HE5050) (B) in three electrode cells at 0^{o}C after completing the formation cycling**.** Cells were fully charged at room temperature prior to performing the measurements.

- As illustrated, the most favorable kinetics at the anode was observed with the cells containing LiDFOB. Whereas, the most facile kinetics observed at the cathode was observed with the cells containing LiBOB and LiBF4 as additives. suggesting that it participates beneficially in the formation of the cathode electrolyte interface (CEI).
- It should be noted that at all temperatures, the kinetics of the cathode are much poorer than that of the anode for all of the samples (by nearly an order of magnitude), suggesting that the low temperature rate capability will be dictated by the cathode kinetics.

Tafel Characterization of Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Jelly Roll Three-Electrode Cells



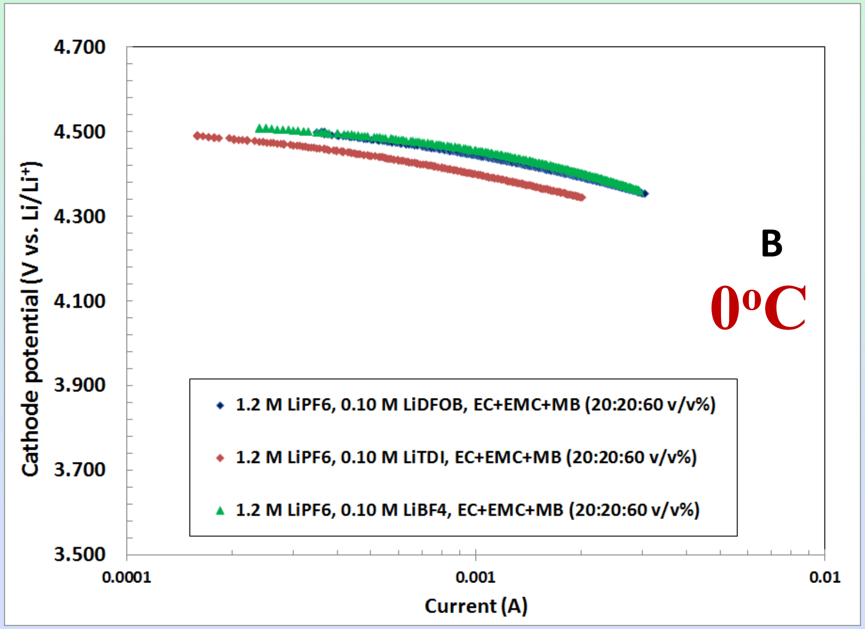
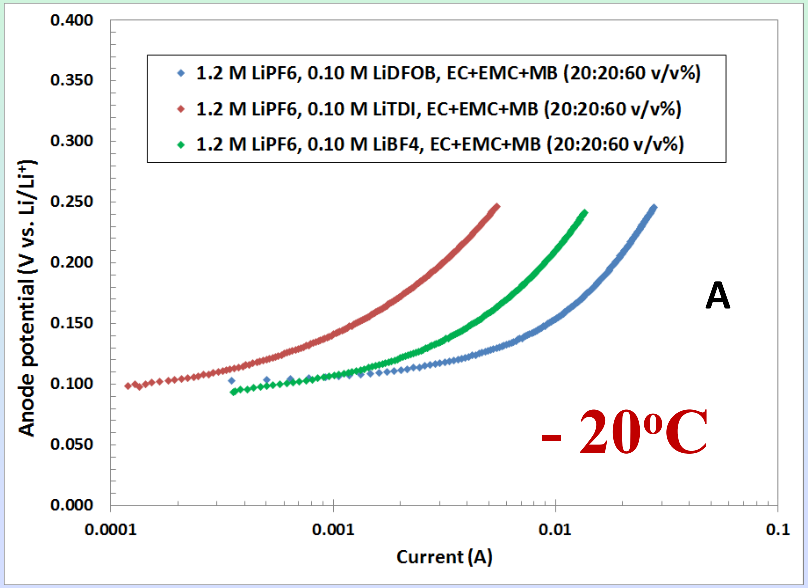


Figure: Tafel polarization measurements performed on Conoco graphite anodes (A) and NMC cathodes (HE5050) (B) in three electrode cells at 0°C after completing the formation cycling**.** Cells were fully charged at room temperature prior to performing the measurements.

- As illustrated, the most favorable kinetics at the anode was observed with the cells containing LiDFOB. Whereas, the most facile kinetics observed at the cathode was observed with the cells containing LiBOB and LiBF4 as additives. suggesting that it participates beneficially in the formation of the cathode electrolyte interface (CEI).
- It should be noted that at all temperatures, the kinetics of the cathode are much poorer than that of the anode for all of the samples (by nearly an order of magnitude), suggesting that the low temperature rate capability will be dictated by the cathode kinetics.

Tafel Characterization of Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Jelly Roll Three-Electrode Cells



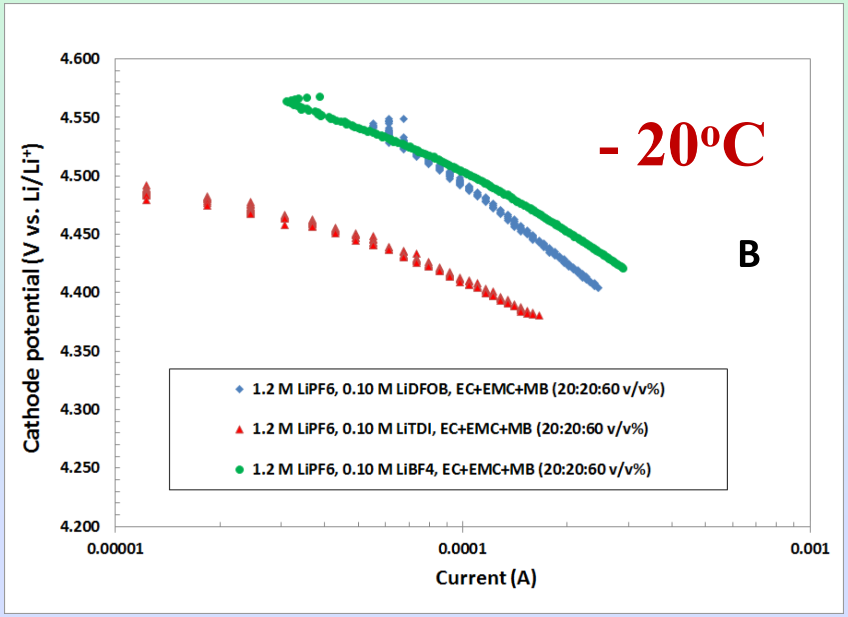
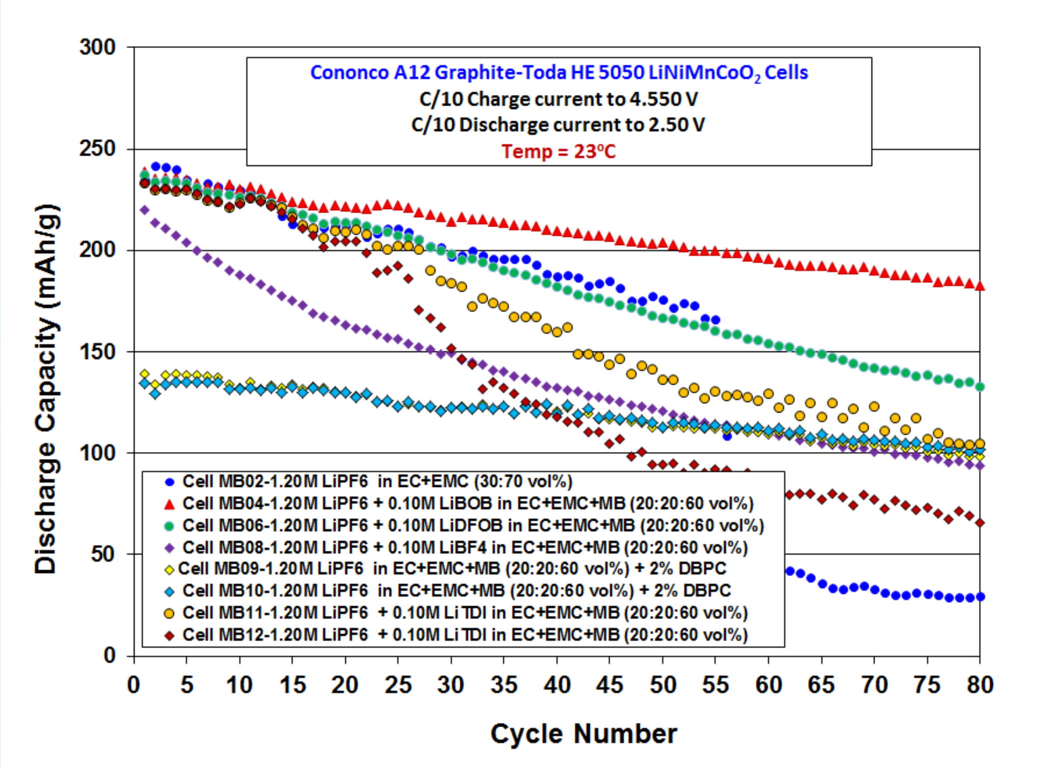


Figure: Tafel polarization measurements performed on Conoco graphite anodes (A) and NMC cathodes (HE5050) (B) in three electrode cells at -20°C after completing the formation cycling**.** Cells were fully charged at room temperature prior to performing the measurements.

- As illustrated, the most favorable kinetics at the anode was observed with the cells containing LiDFOB. Whereas, the most facile kinetics observed at the cathode was observed with the cells containing LiBOB and LiBF4 as additives, suggesting that they participate beneficially in the formation of the cathode electrolyte interface (CEI).
- It should also be noted that at -20°C, the kinetics of the cathode are much poorer than that of the anode for all of the samples (by nearly an order of magnitude), suggesting that the low temperature rate capability will be dictated by the cathode kinetics.

Cycle Life Performance of Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

100% DOD at 23°C (2.5V to 4.55V)

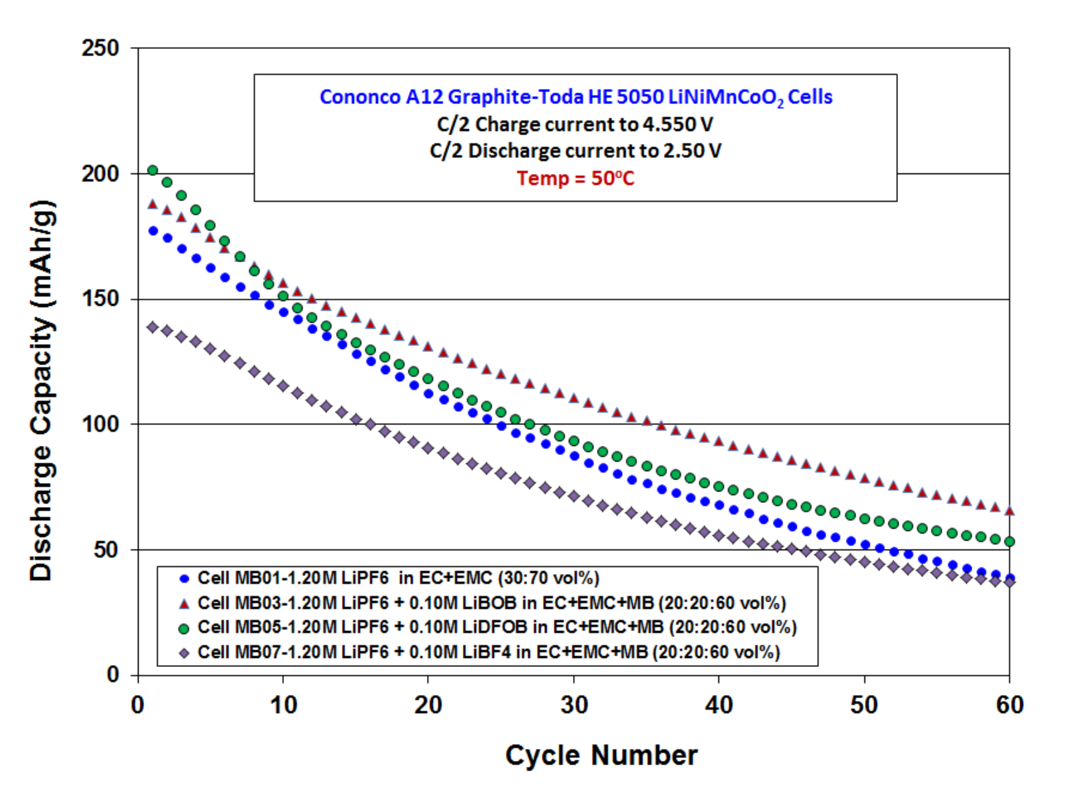


Cycle life performance (100% DOD) on Conoco graphite/$LiNiCoMnO_2$ (HE5050)coin cell at 23°C.

- The cells containing the 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB electrolyte displayed modestly better cycle life performance at 23°C compared with the baseline electrolyte.
- The cells containing the LiDFOB either performed comparably or better than the baseline electrolyte.
- Given that the formulations have been observed to provide dramatically improved low temperature power capability, the fact that they also deliver good cycle life performance, especially at high temperatures, is noteworthy.

Cycle Life Performance of Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

100% DOD at 23°C (2.5V to 4.55V)



Cycle life performance (100% DOD) on Conoco graphite/$LiNiCoMnO_2$ (HE5050)coin cell at 50°C.

- The cells containing the 1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB electrolyte displayed modestly better cycle life performance at 50°C compared with the baseline electrolyte.
- The cells containing the LiDFOB either performed comparably or better than the baseline electrolyte.
- Given that the formulations have been observed to provide dramatically improved low temperature power capability, the fact that they also deliver reasonable cycle life performance at high temperatures is noteworthy.

SUMMARY and CONCLUSIONS

- ***Wide Operating Temperature Electrolytes Demonstrated in Conoco Graphite/ Toda HE5050 $LiNiCoMnO_2$ Cells***
  - *A number of methyl butyrate-based electrolytes have been evaluated in the high voltage LLC-NMC system and compared with a baseline NCA system.*
  - *When Tafel polarization measurements were performed each electrode (using 3-electode cells), both the NCA and NMC electrodes displayed poorer lithium kinetics compared to the anode.*
  - *At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.*
  - *All MB-based solutions outperformed the baseline electrolyte*
  - *A MB-based formulations containing LiBOB delivered good rate capability at low temperature, which is attributed to improved cathode kinetics. However, LiDFOB has recently been demonstrated to provide improved performance at low temperature, which is likely due to preferred anode passivation and resulting characteristics.*
  - *Of the different cathodes, the LLC-NMC electrodes (received from Argonne) displayed much lower lithium de-intercalation kinetics compared to the NCA electrodes (attributed to poor charge transfer resistance of the electrodes), which is exacerbated at lower temperatures.*
  - *At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.*

Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) and Supported by a DOE-BATT-ABR funded program.